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AMBIENT AIR SAMPLING WITH PORTABLE GAS CHROMATOGRAPHS

by

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16. ABSTRACT

A Photovac 10S50 portable photoionization gas chromatograph mounted in a small automobile was used to sample air for organic vapors in Richmond and Hopewell, Virgina and in Staten Island, NY. A methylphenylsilicone column of 1.5 micrometer phase thickness was used with no backflush, and a 10 part per billion mixture of tetrachloroethylene in nitrogen was used as field recalibration standard. Calibrant contamination of the unit was minimal, and background levels of compounds for which the unit was calibrated below 0.5 part per billion could be observed. These compounds were chlorobenzene, ethylbenzene, o-xylene, m-xylene, and bromobenzene. Large releases of benzene, toluene, and several compounds for which the unit had not been calibrated were observed.

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Techniques for monitoring volatile toxic organic compounds in ambient air are often flawed by errors which arise during preconcentration of analytes. It is generally necessary to preconcentrate because ambient levels of pollutants are too low for direct detection. If preconcentration or separation of analytes from the sample matrix could be avoided, such problems could be minimized. An extremely sensitive detector would be required for this, one which could detect concentrations below one part per billion in a conveniently small sample of air. Photovac portable gas chromatographs are commercially available instrument which feature highly sensitive photoionization detectors. They were originally designed for industrial hygiene application, but preliminary laboratory evaluation suggested they were potentially sensitive enough for use in ambient air monitoring. Though negative interferences are minimized, positive interferences are possible since compound identifications are based strictly on chromatographic retention times, so compound identifications are only tentative. However, because sampling is radically less complicated than preconcentration and much less likely to give rise to negative interferences, a response lower than the true ambient level of a target compound would generally not occur. Therefore reported concentrations for target compounds can generally be taken as a credible upper limits to their true concentrations.

A preliminary investigation of the capabilities of the Photovac detector was made using a Model 10A10 chromatograph, and it was apparent that benzene concentrations well below ambient background levels could readily be seen. However, field operation of the 10A10 as a screening device for several compounds was complicated by its lack of data processing capability. Also, it would have been extremely difficult to connect capillary columns to it in field operation. A Model 10S50 instrument which included data processing and capillary column capabilities was then purchased for evaluation. Preliminary laboratory evaluation of the 10S50 showed that it operated as claimed when used to monitor part per million levels of volatile aromatic and haloalkene compounds. Initial attempts to see ambient background levels of these compounds were less successful because pressurized calibration standards on hand at the time were too concentrated for use in the low part per billion range and because capabilities and limitations of the data-processing system were not fully understood. Data are handled by a small built-in computer which detects and integrates peaks, compares peak areas and retention times with library entries, and plots chromatograms and prints quantitation reports on adding-machine tape. Concentrations are reported in parts per million, which is a convenient unit for occupational health work, but not for measuring ambient background levels of organic vapors in air. Library entries are updated periodically by analyzing a field recalibration standard which ideally consists of a known concentration of a single compound in pure balance gas. The observed retention time and response factor for the recalibrant compound are used to correct the corresponding library entry, and all other library entries are modified by the same ratios.

It was assumed that levels of air pollutants in Research Triangle Park were much lower than would be found in any heavily industrialized area. In order to test the Photovac 10S50 in a more polluted area, a trip was made to Houston, Texas during March, 1987. Levels of the compounds for which the unit was calibrated on that occasion, benzene, toluene, vinyl chloride, 1,1-dichloroethylene, trichloroethylene, and tetrachloroethylene, turned out not to be much higher than those found in Research Triangle Park. Field recalibration was done with periodic injection of a mixture of 100 parts per billion each of 1,1-dichloroethylene, trichloroethylene, and tetrachloroethylene in nitrogen. The unit was equipped during this study with a 0.53 X 16 meter fused silica capillary column with a 5 micrometer coating of SE-30 methylsilicone gum rubber which was operated in backflush mode.

Three important problems were encountered during the Houston Study. (1) Calibrant concentration was so high that gain could not be set higher than 100. This produced minimal or zero response to background levels of most compounds. (2) Low-level contamination of the unit by calibrant compounds seemed apparent, and it appeared to be aggravated by the presence of more than one compound in the calibration mixture. (3) Since column temperature was not controlled, retention time shifts often caused peaks to be missed because they eluted outside retention time windows. Because of this, frequent recalibrations were performed during field operation, but they could not entirely solve the problem, since retention times do not vary proportionally with temperature as they do with carrier flow rate.

Because the column enclosure of the Photovac 10S50 was not temperature-controlled, ambient temperatures encountered during field operation have often been significantly different from the temperature at which the calibration library was entered in the laboratory. Field recalibration based on the observed retention time of a single standard compound is the only method available for correcting shifts in retention times. During past field operation at high ambient temperatures it seemed apparent that in spite of recalibration some observed retention times were quite different from corresponding library entries. To test the effects of both carrier flow rate and column temperature, the instrument was calibrated with a mixture of compounds which was produced by blending standard gases in a lecture bottle. Analyses of the blend were performed after one hour, one day, and five days. Concentrations of all compounds were renormalized to the time zero level of tetrachloroethylene. Results are shown in TABLE 1. The concentration of tetrachloroethylene appears constant at its original level while concentrations of the other

TABLE 1. ELAPSED TIME STUDY OF
CALIBRATION MIXTURE CONCENTRATION STABILITY (a)

Elapsed time (hours)	0	19	114
Normalized to Tetrachloroethylene			
1,1-Dichloroethylene	30	24	13
Benzene	159	154	112
Trichloroethylene	34	39	50
Toluene	150	89	67
Tetrachloroethylene	35	35	35
Chlorobenzene	149	66	45
Bromobenzene	151	52	13

(a) Concentrations are in parts per billion by volume.

compounds vary relative to it. The concentrations of tetrachloroethylene and trichloroethylene were reasonably consistent with each other throughout the study, and relative concentrations of 1,1-dichloroethylene and benzene remained fairly stable for at least the first day. These results are consistent with trichloroethylene and tetrachloroethylene concentrations remaining stable while concentrations of the substituted benzene compounds decreased. It appeared that storage stability was poor for toluene, chlorobenzene, and bromobenzene in containers other than the cylinder in which the National Bureau of Standards dispensed Standard Reference Material No. 1811 On the other hand, tetrachloroethylene and trichloroethylene concentrations in lecture bottles have been observed to remain stable over a period of several days when used as field recalibratio standards.

To get an idea of the effect of temperature change between indoor and outdoor conditions in summertime, the mixture of six compounds was analyzed at a flow rate of 20 milliliters per minute and an ambient temperature of 24 C, and the results were used to enter the calibration library. Then the flow rate was changed to 24 milliliters per minute, and a recalibration was done. Bromobenzene was used as the standard. Retention times are shown in TABLE 2. The

TABLE 2. EFFECT OF EXTREME TEMPERATURE SHIFT ON LIBRARY RETENTION TIMES.

	Retention times				
	Original	--Increased Flow--		--High Temperature--	
	Library	Library	Observed	Library	Observed
1,1-Dichloroethylene	27.1	23.2	21.6	23.6 a	15.7
Benzene	63.7	52.2	51.0	46.9 b	37.1
Trichloroethylene	83.9	69.1	67.2	59.9 a	49.0
Toluene	146.1	118.4	116.9	95.9 a	85.0
Tetrachloroethylene	209.3	169.3	167.4	133.1 a	121.9
Chlorobenzene	288.0	231.8	230.4	177.3 a	167.8
Bromobenzene	603.6	483.0	483.0	351.7	351.7
Flow rate (ml/min)	20	24		20	
Ambient temp C	24	24		41	
Unit temp C	31	32		40	

(a) The peak was missed because the library retention time differed from the true retention time by more than five seconds.
(b) The benzene peak was misidentified as trichloroethylene because the library retention time was wrong.

library retention times <u>after</u> recalibration at the new flow rate differed only slightly from the observed retention times. Recalibration using the retention time of a single standard compound is reasonably effective in compensating for changes in retention time due to changes in carrier flow rate so that target compound peaks will fall within a + or - five second window.

This procedure was then repeated outdoors in the shade at an ambient temperature of 41 C. Only bromobenzene, the calibrant, was identified correctly when it was used as the recalibration standard. Other compounds eluted outside their retention time windows. This temperature change was extreme, but it shows that recalibration with a single late-eluting compound does not compensate effectively for changes in retention time due to large changes in column temperature. New library entries were calculated from observed retention times of each compound to determine which would have performed best as a recalibration standard. Results are summarized in TABLE 3. The retention times observed at 41 C and 20 milliliters per minute (first column in TABLE 3) were

TABLE 3. USE OF DIFFERENT COMPOUNDS AS RETENTION TIME STANDARDS (a)

	Retention times (seconds)								
	Observed at 40 C	Original Library	Library retention times revised by normalizing to calibrant retention time						
			1	2	3	4	5	6	7
1 1,1-Dichloroethane	24.2	21.6	24.2 C	21.3 *	20.8 *	19.7 *	19.2 *	18.7	17.7
2 Benzene	50.3	51.0	57.1	50.3 C	49.1 *	46.4 *	45.4 *	44.1	41.9
3 Trichloroethylene	64.7	67.2	75.3	66.3 *	64.7 C	61.2 *	59.8 *	58.1	55.2
4 Toluene	106.4	116.9	131.0	115.3	112.6	106.4 C	104.0 *	101.1	95.9
5 Tetrachloroethylene	148.9	167.4	187.6	165.1	161.2	152.4 *	148.9 C	144.8 *	137.4
6 Chlorobenzene	199.3	230.4	258.1	227.2	221.8	209.7	204.9	199.3 C	189.1
7 Bromobenzene	396.4	483.0	541.1	476.4	465.0	439.6	429.6	417.8	396.4 C

(a) The original library was established at 24 C and 24 ml/min. Then the instrument was run at 41 C and 20 ml/min.
* The observed retention time was within 5 seconds of the revised library retention time.
C This compound was the calibrant for this version of the library.

used to renormalize the library entries created at 24 C and 24 milliliters per minute. The result of normalizing to the observed retention time of each compound is shown in the correspondingly numbered column of the table. Tetrachloroethylene (column 5), if used as recalibration standard would have corrected the retention times of four other compounds adequately to bring them within a + or - five second window (compare column 5 with the left-hand column of retention times observed at 41 C). Toluene (column 4) would also have brought four other compounds within their retention time windows. Of these two compounds, tetrachloroethylene would be the better standard because of its superior concentration stability in dilute mixtures. Use of a column enclosure thermostatted to 30 C could eliminate differences between calibration and field operation temperatures in most cases and would tend to minimize temperature differences which could not be eliminated.

At the request of the Virginia Air Pollution Control Board, an "air sampling demonstration" was conducted during September 14 - 25, 1987 in the cities of Richmond and Hopewell. There had been numerous citizen complaints about air pollution attributed to several chemical plants in the area. Participants in this study included personnel from Virginia Air Pollution Control Board Region 5, EPA Region 3, and EPA Research Triangle Park. Sampling in the Richmond/Hopewell area was conducted on weekdays between Monday, September 14, and Friday September 25, 1987. An EPA van containing transportable sampling and analytical instruments was parked during this time on the southwest bank of the James River in the Richmond Deep Water Terminal. Other transportable sampling equipment was set up in Hopewell on the private property of an Air Pollution Control Board enforcement officer, in plain view about 300 meters from one of the chemical plants. All equipment and gas cylinders used in operating the Photovac 10S50 were transported from Research Triangle Park to Richmond in a Chevrolet Sprint, a compact car with a three-cylinder engine. The Photovac 10S50 was usually operated as a mobile screening unit in the Sprint, which was parked at each sampling site while samples were run. The Photovac was operated on battery power except inside the EPA van. Two external auxiliary gel-cell batteries were used, one being charged while the other was in use. The Photovac internal battery was recharged each night. Carrier air was supplied from the internal storage tank, which was replenished twice each 24 hours. A stainless steel tube was used to conduct outside air to the unit. To avoid contamination, this tube was positioned to project about a meter above the top of the car on the upwind side. While operating the unit in the EPA van the intake tube was connected to the air sampling manifold.

During the Richmond/Hopewell Study a 0.53 millimeter X 15 meter fused silica wall-coated open tubular column with a methylphenylsilicone phase (1.5 micrometers of DB-5) was used without backflush. Carrier flow was 20 milliliters per minute of ultrazero air. The calibration library included chloroethylene, 1,1-dichloroethylene, benzene, trichloroethylene, toluene, tetrachloroethylene, chlorobenzene, ethylbenzene, m-xylene, o-xylene, and bromobenzene. Gas mixtures used in preparing the calibration library were supplied by Scott Specialty Gases, National Bureau of Standards, and Alphagaz. NBS Standard Reference Material No. 1811 was used to establish the library entries for benzene, toluene, chlorobenzene, and bromobenzene. A mixture of 10.9 parts per billion of tetrachloroethylene in nitrogen and air was used as a field recalibration standard. It was produced by making a 10:1 dilution of a 109 part per billion tetrachloroethylene standard with ultrazero air in a lecture bottle. This mixture was supplied to the instrument through a regulator at 15 pounds per square inch (gauge). Mixtures were replaced once during each week, so that they were used for no more than three days. A calibrant concentration of 10.9 parts per MILLION was entered into the microprocessor. This caused all printed concentrations to be 1000-fold higher than true values so that concentrations less than 0.5 part per billion could be reported as decimal fractions larger than zero.

During most of the study the wind should have been sufficient to prevent the instrument from sampling the car. However, it was found that the first sample run at each site often featured larger concentrations than subsequent ones. During the Houston study this was attributed to excessively concentrated recalibrant mixtures containing several compounds. That was certainly no longer a plausible explanation of this continuing problem. Data shown in TABLE 4 are typical. At the beginning of the

TABLE 4. SAMPLING AMBIENT AIR IN HOPEWELL, VA (a)

9-15-87 403 Ramsey Avenue. In front of house. 30 C.

Time	9:39	9:59	10:11	10:31	10:50	11:10
Benzene	*	6.64	*	3.46	2.07	1.09
Trichloroethylene	*	1.38	*	0.26	0.21	ND
Toluene	*	7.58	*	6.20	2.41	1.39
TETRACHLOROETHYLENE	C	1.58	C	1.82	1.11	1.07
Chlorobenzene	*	ND	*	0.35	0.32	0.36
Ethylbenzene	*	1.23	*	0.31	0.15	0.13
m-Xylene	*	2.71	*	1.63	0.64	0.37
o-Xylene	*	ND	*	ND	ND	ND
Total area unknown peaks (volt*seconds)		18.0		44.7	4.09	3.90

(a) Equipped with a 15 m X 0.53 mm WCOT column with 1.5 micrometers of DB-5. 20 ml/min ultrazero air. Concentrations are parts per billion by volume.
ND Not detected.
* Calibration run.
C This compound was the calibrant.

second week of the study an abrupt loss of sensitivity was noticed after changing columns. The sample flow rate, normally 100 milliliters per minute, was monitored with a rotameter and found to be lower than normal and falling. A sample flow rate below 60 milliliters per minute could not sweep the 10 milliliter loop during a 10 second sampling period, and the flow had fallen to 38 milliliters per minute. The mystery was not that only a few peaks were seen but that any were seen at all. Sampling was discontinued until the problem could be remedied. Before returning the unit to service, the sampling system was carefully inspected. No leaks or blockages were found. The sample pump was disassembled and checked for a torn diaphragm or plugged ports. A tiny quantity of fuzz was removed from the ports, but it did not appear sufficient to cause the problem, and removing it did not immediately improve the flow rate. The long narrow-bore sample loop which had been installed was replaced with the original short large-bore sample loop, whereupon sample flow rate rose to about 45 milliliters per minute. During the rest of the study a 45 second sampling interval was employed, and sample flow rate was monitored continuously with a rotameter. It never fell below 45 milliliters per minute. This mode of operation caused more than 33 milliliters of air to be drawn through the 10 sample loop. After this change in procedure levels in the first sample of each set were no longer significantly higher than in subsequent ones. No specific cause for the loss of sample flow rate was ever identified; a leak was suspected, but never found. Sample flow rate eventually returned to normal after further plumbing changes were made, and it was monitored with a rotameter in subsequent work.

At this point it seemed prudent to check the condition of the calibration library. Since field recalibration corrects library entries by multiplying them by calculated ratios, significant errors might arise after numerous recalibrations, especially with large changes in retention time. To check for this, all library entries were compared with responses to calibrant mixtures and then replaced with correct concentrations and retention times. It was found that response factors had drifted slightly upward, and retention times in the new library were lower than in the old one, especially for the less-volatile compounds. Apparently lack of column temperature control is likely to be a more significant source of error in library entries than low-precision arithmetic in the microprocessor. The observed changes in library retention times, though not large, were sufficient for the heavier compounds to be missed on most runs.

After the calibration library had been replaced, response to the old field recalibration mixture was compared with response to the new one. The old mixture was used to recalibrate repeatedly until a steady response of 10.9 parts per billion was attained. Then the new standard was prepared and sampled. The response of 10.15 parts per billion for the new standard was in good agreement with the old standard and suggested that errors in measuring pressure while preparing the mixture were probably more significant than loss of tetrachloroethylene during a three day period. This is consistent with past experience which has shown that trichloroethylene and tetrachloroethylene calibration mixtures are stable over periods of a few days.

After redoing the library, a series of samples were taken at the south end of Commerce Street in Richmond. The site was chosen primarily because it was downwind of a chemical plant which was about 500 meters to the west. Data taken at this site are shown in TABLE 5. The first two

TABLE 5. SAMPLING AMBIENT AIR IN RICHMOND, VA (a)

9-24-87 South end of Commerce Street. 500 m downwind of du Pont. 27-23 C.

Time	18:46	19:07	19:26	19:33	19:51 (b)	20:13	20:33 (c)	20:49
Benzene	*	0.77	0.87	*	7.17	*	64.1	72.5
Trichloroethylene	*	ND	ND	*	ND	*	6.24	7.10
Toluene	*	2.46	3.90	*	12.5	*	47.4	47.0
Tetrachloroethylene	C	0.36	0.48	C	0.19	C	ND	ND
Chlorobenzene	*	0.26	0.14	*	0.12	*	ND	ND
Ethylbenzene	*	ND	ND	*	ND	*	ND	ND
m-Xylene	*	ND	ND	*	ND	*	ND	ND
o-Xylene	*	ND	ND	*	ND	*	ND	ND
Gain	200	200	200	200	200	100	100	100
Total area unknown peaks (volt*seconds)		5.14	2.42		10.38 (b)		42.3 (c)	30.5

(a) Equipped with a 15 m X 0.53 mm WCOT column with 1.5 micrometers of DB-5. 20 ml/min ultrazero air. Concentrations are parts per billion by volume.
ND Not detected.
* Calibration run. This compound was the calibrant.
(b) Cannister N-3 was filled.
(c) Cannister NQ-4 was filled.

samples were not exceptional. The third showed sudden increases in benzene and toluene, so the instrument was recalibrated at lower gain. The last two samples showed the highest levels of benzene and toluene seen during the study. They also indicated a substantial level of trichloroethylene. Several large unidentified peaks were also present, which may have been xylenes. This sampling was done just after sundown, and rapidly falling temperature made it difficult to keep the less volatile compounds inside their retention time windows.

During the Richmond/Hopewell Study, Monitoring Methods Section (MMS) and contractor personnel were collecting whole air samples in six-liter Summa Polished cannisters and analyzing them for volitile organic compounds. Cryogenic preconcentration was followed by temperature-programmed chromatography using tandem flame ionization/photoionization detectors and an electron capture detector. Eleven cannisters were filled at the same times and places where Photovac samples were taken. Two of these were filled at the Commerce Street site. Cannister ports were held within 5 centimeters of the Photovac sample inlet. In general there was reasonably close agreement betwee cannister and Photovac results. Most discrepancies resulted from the Photovac missing peaks because of shifts in ambient temperature. TABLE 6 summarizes the differences between

TABLE 6. Average Differences between Photovac and Cannister Responses.

Site	Number of Compounds Found			Average Difference	High Method
	Cannister	Photovac	Both		
Hopewell, Hardee's	5	5	3	0.3	NONE
Hopewell, VA-10 at W. Churchill Drive	7	7	6	4.1	PV
Hopewell, VA-10 at W. Churchill Drive	6	5	5	2.2	PV
Hopewell, Harrison Point	6	3	2	1.5	CAN
Hopewell, Shirley Plantation	5	5	4	1	PV
Hopewell, Jordan Point	4	6	4	1.3	NONE
Hopewell, Shirley River Bank	5	0	0		
Hopewell, Harrison Point	6	0	0		
Richmond, Commerce Street	6	4	3	2.7	PV
Richmond, Commerce Street	7	3	2	36.9	PV
Hopewell, VA-10	5	5	4	38.6	NOT

Photovac and cannister results. Only compounds for which both methods were calibrated have been listed in the table. The number of compounds identified by each method are shown, as well as the number found by both methods. The average absolute concentration differences (in units of parts per billion) are shown. Better chromatographic resolution was achieved in analyzing the cannister samples because temperature programmed chromatography was used, and the results were less subject to positive interferences, though not entirely free of them. Because of positive interferences, Photovac responses generally should be higher, and in most cases they were. In all but two cases there was good agreement between the two methods. In both cases where there was not, a rapid increase in pollutant concentrations was in progress at the time the samples were taken, as shown by consecutive Photovac runs. In the last and worst case, the Photovac and cannister samples were not simultaneous, the cannister having been filled one minute after the Photovac sample was taken.

TABLE 7. SAMPLING AMBIENT AIR IN STATEN ISLAND, NY (a)

10-21-87 Room 457, Susan Wagner High School, 50 Brielle Avenue, New York, NY
Sampler was connected to a manifold which was importing outdoor air.

TIME	BENZENE	C13-ETHENE	TOLUENE	C14-ETHENE	C1-BENZENE
004	0.72	ND	14.6	0.07	ND
019	0.72	ND	14.2	ND	ND
049	0.70	ND	16.2	0.05	0.04
104	0.70	ND	14.5	ND	0.07
134	0.68	ND	15.8	0.19	ND
149	0.75	ND	15.3	0.17	ND
219	0.72	ND	15.8	0.30	ND
234	0.80	ND	15.5	0.34	ND
304	0.74	0.12	18.4	0.68	ND
319	0.78	ND	20.0	0.21	ND
349	0.91	ND	23.7	ND	ND
404	1.16	ND	22.8	ND	ND
434	1.47	ND	28.5	0.24	ND
449	1.51	0.07	30.4	0.30	ND
519	2.02	0.14	31.1	0.39	ND
534	1.94	0.09	30.1	0.07	ND
604	1.93	0.09	26.9	0.03	ND
619	1.90	0.09	22.4	ND	ND
649	1.85	ND	22.5	ND	ND
704	2.12	ND	21.1	ND	ND
734	2.11	0.08	20.9	ND	ND
749	1.88	0.03	19.8	ND	ND
819	3.22	ND	20.8	0.34	ND
834	2.30	0.04	18.2	0.32	ND
904	3.07	ND	19.2	0.39	ND
919	3.65	ND	12.6	ND	ND
949	2.95	0.10	21.1	0.27	ND
1004	3.29	0.13	21.3	0.29	ND
1034	2.63	0.04	20.6	0.48	ND
1049	2.34	ND	18.4	0.52	ND

(a) Concentrations are in parts per billion by volume.

In preparation for the Richmond/Hopewell, study the Photovac was calibrated for vinyl chloride and 1,1-dichloroethylene in addition to the compounds which are listed in the tables. On every run several very large early-eluting peaks "buried" these compounds. When reported by the microprocessor, they were usually perceived at part per million levels. Such results were not credible. Furthermore, cannister sample reports generally showed substantial quantities of early-eluting hydrocarbons and freons. In no case was a Photovac report of a large quantity of vinyl chloride or 1,1-dichloroethylene corroborated by a cannister report. It is not reasonable to suppose that the cannister method performed less well for these two highly volatile compounds than for less volatile compounds. The reasonable conclusion is that Photovac results for these two compounds were unreliable because the column was not suitable to analyze them. In a few cases the cannister method found higher concentrations than the Photovac. Even so, the results were similar, and frequently the difference between the two quantitation lists appeared to be a simple ratio which could have arisen from minor calibration errors. In many cases the cannister method saw compounds eluting after tetrachloroethylene when the Photovac did not. In view of the column temperature problems which afflicted the Photovac, that was not surprising.

The Photovac 10S50 was operated as part of the Staten Island Shoot-Out Study during October 20 - 22, 1987. During this period the unit was operated mostly as an unattended sampler. Some of the data are shown in TABLE 7. During this study the Photovac was operated indoors, sampling outdoor air which was being imported through a manifold by a suction fan. As before, the unit was equipped with a fused-silica 0.53 millimeter X 15 meter wall coated open tubular column with 1.5 micrometer DB-5 methylphenylsilicone stationary phase, carrier flow was 20 milliliters per minute of ultrazero air, and recalibration was done with a 10.9 parts per billion of tetrachloroethylene in nitrogen and ultrazero air. The compounds reported were those for which the unit had previously produced consistently credible results with the DB-5 column. The five compounds reported are benzene, trichloroethylene, toluene, tetrachloroethylene, and chlorobenzene. The unit was operated at a single indoor location where the temperature varied from 22 to 27 C. This range was narrower than usual for field operation. During the period these samples were taken the wind gradually increased to perhaps seven or eight miles per hour and shifted from the southwest to the west. Approximate outdoor temperatures ranged from 5 - 18 C. The sky was heavily overcast, and humidity was very high.

In previous work the unit had shown a tendency to calibrate on the wrong peak. This had precluded unattended operation at high gain. Even the cleanest calibration mixture displays extraneous peaks at high gain, and since the 10S50 chooses the calibrant peak on the basis of elution order, any variation in the number of peaks can cause it to calibrate with the wrong one. A calibrant flow time of one or two seconds had been used, consistent with manufacturer's recommendations. Longer times were avoided to conserve calibrant. Since calibrant was being diluted 10:1 with ultrazero air and had to be discarded after three days, conserving it was no longer important, so flow times of five or ten seconds were tried. They resulted in dramatic reduction of extraneous peaks on the calibration chromatogram, and accidental calibration on the wrong peak was correspondingly diminished. Apparently most of the extra peaks came from slight contamination of the pressure regulator. No wrong peak was ever hit during the first night of unattended operation. On the second night wrong peaks were hit on about half the calibration runs. That meant about half the data were spoiled, but it was still a drastic improvement on past performance. Clearly it is desirable that the sample loop be thoroughly flushed out by both sample and calibrant when operating in the part per billion range. This is much more important than it is at part per million levels.

Future work will be directed to evaluation of the constant-temperature column enclosure and software upgrades which are now being offered by the manufacturer. It is hoped they will make possible use of the unit for screening larger numbers of compounds under more extreme temperature conditions.